



Photocatalytic degradation of olanzapine in aqueous and river waters suspension of titanium dioxide

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ABSTRACT

The photostability of olanzapine, recently most commonly used atypical antipsychotic agent, was investigated. Two irradiation sources were applied, namely solar simulated light ($E = 250$ and 500 W/m^2) and monochromatic ultraviolet light ($\lambda = 254$ and 366). The olanzapine adsorption on a titanium dioxide surface was confirmed by differential scanning calorimetry and infrared spectroscopy. Kinetic studies were performed on a basis of a spectrophotometric method. Degradation efficiency was assessed by applying high performance liquid chromatography with an ultraviolet detection. HPLC analysis did not show any degradation products. Olanzapine was found to degrade under photocatalytic conditions with the creation of low molecular products. Disappearance of olanzapine from titanium dioxide surface after degradation was confirmed by IR spectra. A simple and promising way to apply the photocatalytic removal of olanzapine in titanium dioxide suspension was presented.

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1. Introduction

Olanzapine (2-methyl-4-(4-methyl-1-piperazinyl)-10H-thieno [2,3-b][1,5]benzodiazepine, OLA, [Scheme 1](#)) is a widely used psychotropic drug [1]. It was introduced into commercial use in 1996 in over 84 countries [2]. At present OLA is a top-ten best-seller drug marketed by Eli Lilly & Co. [3]. In the United States it is the most commonly used atypical antipsychotic agent [4]. This is mostly due to its high therapeutic efficiency in the treatment of both schizophrenia and bipolar disorder [5].

Atypical antipsychotics seem to be more effective than classic neuroleptics, such as phenothiazines and butyrophenones, because they can suppress both positive and negative symptoms of schizophrenia. Classic neuroleptics are active only against positive symptoms of the illness. What is more, OLA causes fewer extra-pyramidal side effects than the classic drugs [6,7].

It should be stressed that OLA is a representative of multi-target drugs. It binds to more than a dozen receptors for serotonin, dopamine, muscarine, noradrenaline and histamine. This kind of profile would normally be unacceptable, but the OLA has been highly effective in the treatment of psychotic disorders [8]. This so-called promiscuous ligands or dirty drugs are going to displace a combination therapy owing to its disadvantages, which are the number of different medications and the associated dose regimens. Combination therapy consists in administering two or more drugs

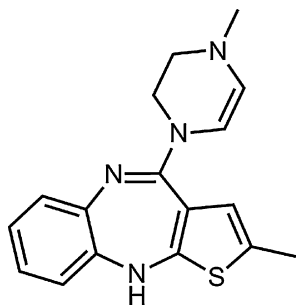
showing selectivity against the different targets, whereas promiscuous ligand can simultaneously interact with a range of targets [9].

Because of a common usage of the OLA and its promising application in the treatment of psychiatric diseases, relatively huge amounts of this pharmaceutical are used. In recent years, pharmaceutical residues have appeared as a new class of pollutants in the environment, mainly as a consequence of emission from production sites, disposal of unused or expired products, excretion after application for human and animal medical care and as a result of therapeutic treatment of livestock on fields [10]. These substances and their metabolites may accumulate in soils and sediments and contaminate groundwater, or be discharged into sewers through urine and faeces and then enter sewage-treatment plants (STPs), prior to entering rivers, streams, lakes and sea. Sometimes, not only the parent compound may arouse adverse effects on ecosystem and human health but also its metabolites. For most medical substances and their metabolites the transformation pathways in the aquatic system are largely unknown and investigations of their occurrence in the environmental compartments are still rare [11].

OLA has been already determined in human body fluids, including plasma [12], serum [1], urine [13] and breast milk [12] at the following concentrations: 24 ng/mL , up to 75 ng/mL , 6.99 ng/mL and 12.2 ng/g . What is more OLA concentration was examined post-mortem in fluids like heart blood, femoral blood, urine, spleen and different organs including liver, brain, kidney, heart and lung [14]. The OLA concentrations in above mentioned samples were as follows: 1.38, 1.11, 60.24, 2.78, 6.47, 2.13, 2.39, 1.72, 38.36 ng/mL , respectively. Antipsychotics (diazepam [15] – 1.2 µg/L) and other

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Scheme 1. Chemical structure of olanzapine.

neuroleptic drugs (carbamazepine [16] – 0.7 µg/L) were also found in river waters. However, no studies concerning OLA presence in river waters were found by the authors.

Heterogeneous photocatalysis represents an example of advanced oxidation processes able to achieve a complete oxidation of inorganic [17,18] and organic [19,20] species, including also pharmaceutical substances [21,22]. It takes advantage of some semiconductor solids, which can be used as photocatalysts suspended in the water effluent to be treated, or immobilized on various types of supports. Among them, TiO₂ is widely used because it is non-toxic, inexpensive, as well as biologically and chemically inert. The electron/hole pair (e⁻/h⁺), generated under light illumination of energy greater than 3.2 eV, reacts with the molecules, objects of degradation, or water molecules oxidized by the photoholes (h⁺) and gives rise to the generation of hydroxyl radicals, responsible for the complete decomposition of the chemical substances.

Degradation of the OLA in acidic, basic, oxidizing and photolytic conditions as well as under thermal stress was investigated by others [23,24]. It was proved that OLA does not degrade under UV radiation at 254 nm. It is also stable in oxidation conditions, whereas in acidic and basic pH it starts to degrade after 30 min. Furthermore, some pharmacokinetics analysis of OLA were performed and already described [1,23,25]. However, no investigations concerning photocatalytic degradation of this pharmaceutical were carried out so far.

In the present work, the photodegradation of OLA in the presence of a catalyst, namely TiO₂, in water and river solutions was investigated. Two sources of irradiation: ultraviolet lamp and solar light simulator were applied. The parallel experiments without addition of catalyst were conducted too. We aimed at determination of possible intermediate products of photodegradation process. We wanted to get to know the process of OLA decomposition in the environment of river waters and assess the possibility of application the photocatalysis as a way of decontamination of river waters.

2. Experimental

2.1. Materials and reagents

TiO₂ (anatase) was purchased from Sigma–Aldrich. Olanzapine was obtained from 5 mg Zalasta tablets, which were purchased as available on the market and prescribed for human patients. Stock solution was prepared by dissolution of three crushed Zalasta tablets in sulfuric acid and further filtration. It was diluted with deionized water into a working concentration (5 × 10⁻⁵ mol/L) before each experiment [26–28].

Absolute methanol, disodium hydrogen phosphate, hydrochloric acid, orthophosphoric acid, sodium hydroxide, sodium carbonate, sodium hydrogen carbonate, sulfuric acid (all POCh, Gliwice, Poland) and ammonium reineckate – NH₄[Cr(SCN)₄(NH₃)₂]·H₂O

(BDH Chemicals Ltd., England) were used. All above mentioned chemicals were analytical grade reagents and used without further treatment. HPLC-grade acetonitrile was purchased from Merck. All solutions were prepared using deionized water, which was obtained by Polwater apparatus.

2.2. Photocatalyst characterization

Differential scanning calorimetry (DSC) analyses were performed by a Thermal Analyzer DSC 1 (METTLER TOLEDO) with a heating rate of 10 °C/min under air environment with flow rate = 200 mL/min. All runs were carried out from 0 °C to 500 °C and reverse cycles from 500 °C to 0 °C were registered too. The measurements were made in open aluminum crucibles, nitrogen was used as the purge gas in ambient mode, and calibration was performed using an indium standard.

ATR-IR spectra were recorded from 4000 to 500 cm⁻¹ using a Thermo Scientific Nicolet™ 6700 spectrometer with 32 accumulations at a resolution of 4 cm⁻¹. This instrument was equipped with a KBr beamsplitter, an ETC source and a DTGS detector.

2.3. Spectrophotometric analyses

UV spectrophotometric analyses were performed using a HITACHI U-2800A UV–vis spectrophotometer equipped with a double monochromator and a double beam optical system (190–700 nm) in 1 cm quartz cell. Absorbance was recorded in the range of 190–400 nm, and the maximum absorption wavelength experimentally registered at λ = 256 nm was used for the calibration curve and further OLA concentration measurements.

Photolytic as well as photocatalytic degradation experiments were carried out in a solar simulator apparatus, namely SUNTEST CPS+ (Atlas, USA), and upon UV irradiation using UV-Standard lamp (220–240 V, 50–60 Hz, 16 VA, Cobrabid) capable of emitting monochromatic radiation of 254 and 366 nm. The photon flux of ultraviolet and solar simulated radiation was measured by chemical method – Reinecke's salt actinometer [29]. The photon flux of UV light of 254 and 366 nm was 1.28 × 10⁻⁷ and 1.12 × 10⁻⁷ Einstein/s, whereas intensity of solar simulated light of 250 and 500 W/m² was 2.18 × 10⁻⁶ and 2.32 × 10⁻⁶, respectively. As a UV filter window glass with a cut-off at 320 nm was used.

The experiments were performed in 50 mL glass cell. The reaction mixture consisted of 20 mL of OLA sample (5 × 10⁻⁵ mol/L) and TiO₂ (1.56 g/L) as a photocatalyst. Prior the irradiation the pharmaceutical-catalyst suspension was kept in the dark with stirring for 1 h to ensure an adsorption–desorption equilibrium. To determine the OLA degradation, the samples were collected at regular intervals (15 min) and centrifuged to remove the photocatalyst.

2.4. Chromatographic conditions and equipment

The chromatographic experiments with HPLC–UV system were carried out on a Varian 920 liquid chromatograph using a quaternary solvent pump and an autosampler. The chromatographic column used Lichrospher® 100 RP-18 125 mm × 4.6 mm packed with 5 µm particle size. Separation was achieved using a linear gradient method. The mobile phase consisted of two solutions namely A and B. Solution A was prepared from 10 mmol/L disodium hydrogen phosphate, pH adjusted to 7.4 with orthophosphoric acid, whereas solution B was acetonitrile. The initial ratio of A:B was 70:30 (v/v). The gradient was as follows: 0 min, 70% A; 15 min, 70% A; 25 min, 20% A; 30 min, 20% A; 35 min, 70% A; 40 min, 70% A. The column was equilibrated for 10 min before performing the next injection. The flow rate of the mobile phase was 1 mL/min and the injection volume was 100 µL. The column was maintained at a room temperature. The eluent was monitored at 256 nm.

Table 1
LOD, LOQ and regression data.

Parameter	LOD (mol/L)	LOQ (mol/L)	Slope (<i>b</i>)	Intercept (<i>a</i>)	<i>R</i> ²
Value	2.29×10^{-6}	6.86×10^{-6}	−0.55	621,970	0.9997

Before irradiation studies a standard curve of OLA was obtained in order to ensure that peak registered for 5×10^{-5} mol/L concentration of OLA in fact corresponds to examine pharmaceutical agent. By injecting solutions of known concentrations, based on the standard deviation (σ) of the response and the slope (*b*) of the calibration plot and using the formula $\text{LOD} = 3.3\sigma/b$ and $\text{LOQ} = 10\sigma/b$, the LOD and LOQ for OLA were estimated (Table 1). Chromatograms of the following concentrations of OLA were registered in Fig. 2: 10^{-7} , 2×10^{-5} , 4×10^{-5} , 5×10^{-5} , 6×10^{-5} , 8×10^{-5} mol/L.

2.5. River water quality parameters assessment

River water quality parameters that can affect the photodegradation process of examined pharmaceutical were measured. They included: pH, general hardness, calcium, magnesium and chloride concentrations as well as chemical oxygen demand, acidity, alkalinity, dissolved oxygen, conductivity and iron concentration. All above mentioned chemical parameters were measured according to appropriate standard method and presented in Table 2 [30]. Most of those parameters of examined river water samples were within acceptable values.

3. Results and discussion

3.1. The primary studies

As presented in Fig. 1, the absorption spectrum of OLA in neutral environment is characterized by one main band in the ultraviolet region at $\lambda = 256$ nm. Spectrum in the basic solution differs from those in neutral and acidic pH. It possesses two additional bands at 196 and 222 nm. Influence of the pH on the photocatalytic degradation of OLA will be discussed later.

No photolytic degradation of neutral aqueous solution of OLA by UV light of 366 nm neither by solar simulated light of 250 W/m² has been observed during 2 h of irradiation.

3.2. Adsorption character studies

3.2.1. Spectrophotometry

Adsorption studies were performed in order to estimate whether the adsorption of OLA on the TiO₂ surface has physical or chemical character. It is well known that physisorption is well

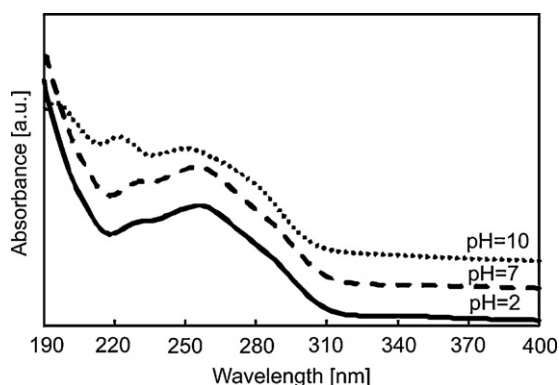


Fig. 1. Absorption spectra of aqueous solution of olanzapine (5×10^{-5} mol/L).

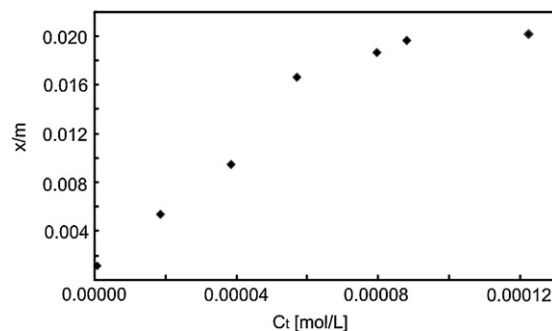


Fig. 2. Isotherm of the adsorption process of OLA on the photocatalyst surface.

described by the Freundlich isotherm, whereas chemisorption – by the Langmuir isotherm.

Experimental data were fitted to the plot of x/m versus C_t and presented in Fig. 2.

Relationship showed in Fig. 2 is typical for the adsorption process. It is clear that with an increase in OLA concentration there is also, to some point, an increase in mass of OLA which is adsorbed on the TiO₂ surface. However, after crossing enough high concentration value no more adsorbate is able to be adsorbed on the adsorbent surface. Unfortunately, presented chart does not directly indicate the adequate adsorption character. In order to determine that, linear relationship is crucial. With the aim of doing that, the linear transformations of Freundlich and Langmuir isotherms were expressed by the following equations:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C_t \quad (1)$$

$$\frac{C_t}{x/m} = \frac{1}{k(x/m)_\infty} + \frac{C_t}{(x/m)_\infty} \quad (2)$$

where x is the mass of OLA adsorbed on the photocatalyst surface, m is mass of TiO₂, C_t is concentration of OLA in the solution after 1 h of adsorption in the dark, k is adsorption constant, n is constant characteristic for an exact system.

To establish the adsorption character experimental data were fitted to both above mentioned equations (Eq. (1) and Eq. (2)) and showed in Fig. 3.

Higher value of a correlation coefficient in case of Freundlich isotherm ($R^2 = 0.9749$) in comparison with that in Langmuir isotherm ($R^2 = 0.7755$) was obtained. Therefore, we concluded that the adsorption is well described by a Freundlich type isotherm. Those results suggest physisorption.

3.2.2. Differential scanning calorimetry (DSC)

DSC curves of TiO₂, OLA and TiO₂ after adsorption of OLA were registered (Fig. 4). The DSC curve of OLA showed a sharp endothermic peak at 200 °C, which is typical for that pharmaceutical. However, above mentioned peak is not observed on the DSC curve of TiO₂ after adsorption of OLA without further irradiation. Therefore, the DSC curve of TiO₂ after adsorption of OLA differs from the DSC curve of a bare TiO₂, what indicates the presence of a pharmaceutical on a photocatalyst surface as a consequence of an adsorption. It should be mentioned, that the lack of major changes between the first and the third curve may be the consequence of different values of heat flow in TiO₂ and OLA. Photocatalyst is resistant to temperature influence in applied temperature ranges.

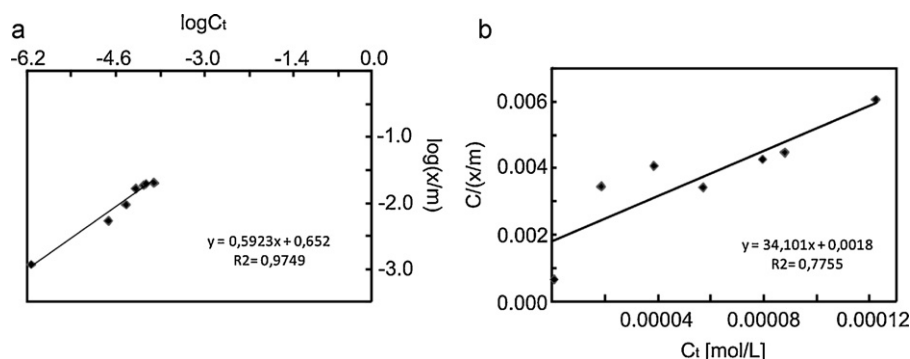
3.3. Effect of catalyst loading

3.3.1. Adsorption

The relationship between a catalyst dose and a decrease in the concentration after adsorption was examined. An increase in

Table 2
River water quality parameters.

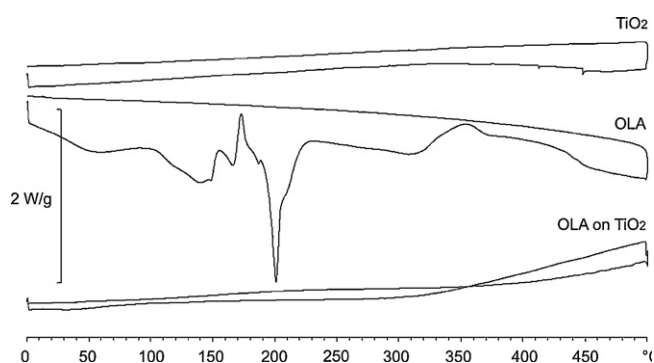
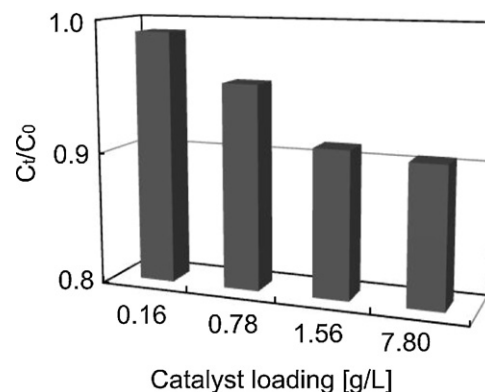
	Method	Marycha	Narew	Norms
pH	pH meter	7.79	7.39	6.5–8.5
General hardness (°dH)	EDTA titrimetric	25.94	19.77	6–30
Calcium (mg/L)	EDTA titrimetric	175.25	150.20	<250
Magnesium (mg/L)	EDTA titrimetric	47.27	20.54	<150
Chloride (mg/L)	Mohr method	122.89	141.80	0.4–170
Chemical oxygen demand (COD) (mg/L)	Potassium manganate method	2.60	3.37	<25
Acidity (mval/L)	Acidimetry	5.27	4.43	–
Alkalinity (mval/L)	Alkalimetry	0.24	0.43	–
Dissolved oxygen (%)	Winkler method	61	73	>70
Conductivity (μS/cm)	Conductivity meter	34	29	–
Fe (mg/L)	Spectrophotometry	0.29	0.23	<0.5

**Fig. 3.** Linear Freundlich (a) and Langmuir (b) adsorption isotherm of OLA on the photocatalyst surface.

catalyst loading resulted in a decrease in OLA concentration after adsorption. However, after crossing sufficiently high value of loading no more further decrease in OLA concentration is observed. Therefore, the ratio of OLA concentrations before and after adsorption (C_t/C_0) decreased with increasing of a catalyst loading in the following order $0.16 > 0.78 > 1.56 > 7.8$ g/L (Fig. 5). But 7.8 g/L load of a catalyst led to approximately the same C_t/C_0 ratio as was obtained at application the lowest catalyst dose (0.16 g/L). Following these observations, the amount of TiO_2 was kept constant at the optimal load of 1.56 g/L in all the subsequent photocatalytic degradation experiments.

3.3.2. Photodegradation

The influence of the catalyst loading on the photodegradation process was studied too. Kinetic values (k_{app} and $t_{1/2}$) at varying catalyst loading were calculated and presented in Table 3. An increase in k_{app} with a decrease in $t_{1/2}$ values was observed when the catalyst loading was increased. However, the higher catalyst loading was applied the smaller increase in k_{app} and a decrease in $t_{1/2}$ were observed.

**Fig. 4.** DSC curves of TiO_2 , OLA and TiO_2 after adsorption of OLA.**Fig. 5.** OLA concentration decrease after 1 h of adsorption as a function of a catalyst loading.

It can be ascribed to the two opposed contributions to the degradation process that the load of a catalyst makes. On the one hand, high catalyst loading makes available a higher number of active sites for adsorption on the surface of the particles, but on the other hand the amount of light dispersed by the catalyst particles is higher. These particles are therefore not available for generation of h^+/e^- pairs, and part of the originally activated TiO_2 may also be deactivated through collision [21].

Table 3

Pseudo-first order rate constants k_{app} and half-live times $t_{1/2}$ for photocatalytic degradation of OLA upon irradiation with solar simulated light (250 W/m^2) at varying catalyst loading (g/L).

Catalyst loading (g/L)	k_{app} (min^{-1})	$t_{1/2}$ (min)
0.16	0.0077	90
0.78	0.0083	84
1.56	0.0103	67
7.8	0.0113	61

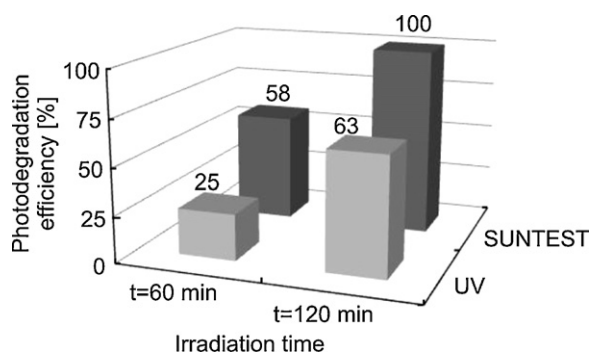


Fig. 6. Photodegradation efficiencies obtained after 60 and 120 min of aquatic solutions of OLA irradiation using ultraviolet (UV) and solar simulated light (SUNTEST).

Following these observations, the amount of TiO_2 was kept constant at the optimal load of 1.56 g/L in all the subsequent photocatalytic degradation experiments.

3.4. Photocatalytic studies

Studies concerning photocatalytic degradation of OLA were performed in a suspension of TiO_2 . Photodegradation efficiency of examined solutions was tested using two sources of irradiation, namely monochromatic ultraviolet and solar simulated light. Results obtained for aquatic solutions of OLA were presented in Fig. 6. They proved that solar simulated light leads to complete degradation of OLA after 2 h of irradiation, while photodegradation efficiency with the use of ultraviolet light amounted to 64%. It can be assumed that 1 and 2 h of irradiation using ultraviolet and solar simulated light lead to the similar results.

Fig. 7 shows the OLA absorption spectra during the photodegradation reaction. The disappearing peak at 256 nm in the UV-spectra indicates a degradation of the OLA molecules. No additional peaks occur at the spectra. However, the position of the maximum was found to shift to higher wavelengths with the irradiation time. What is more, an increase of a base line with the wavelength decrease was observed. Therefore, we concluded that some species with low molecular weight may be dissolved in the water. TOC analysis proved those hypotheses, because no noticeable decrease in TOC concentration was found.

Further chromatographic analyses were performed. Registered chromatograms (Fig. 8) also did not show any intermediate products. After 2 h of irradiation only a decrease in OLA peak was observed. It is presumed that the reason of those results is a UV detector which is not able to detect those low molecular species.

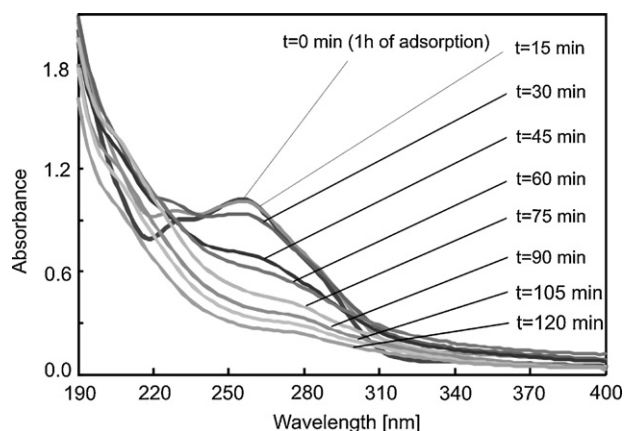


Fig. 7. UV-spectra changes of OLA in aqueous solutions with the increasing irradiation time.

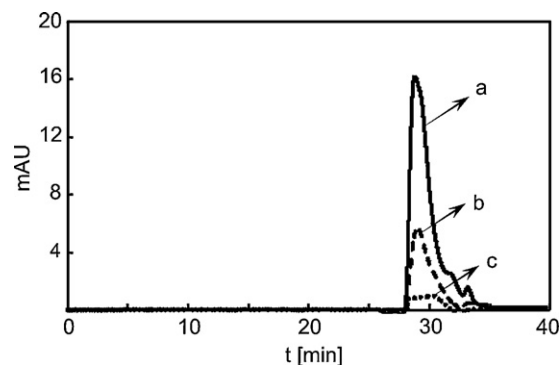


Fig. 8. Chromatograms of OLA (a) before and after 2 h of solar simulated light (SUNTEST) (b), and ultraviolet light (UV) irradiation (c).

Infrared spectroscopy also confirmed OLA degradation after irradiation. Spectra of TiO_2 , OLA, TiO_2 after adsorption of OLA and TiO_2 after OLA degradation were registered and presented in Fig. 9. Wave numbers in OLA spectrum as follows: 1581.56, 1422.44, 1257.64, 1217.86, 1112.72, 1030.32, 754.70 correspond to N–H, O–H, C–H, C=O, C=C, C=N and C–N stretching, respectively [31]. Spectrum of TiO_2 after 1 h of adsorption indicates that OLA was adsorbed on its surface. It was proved on the basis of the appearance of 5 additional peaks which were not observed in TiO_2 spectrum. Those peaks disappeared after 2 h of irradiation under solar simulated light. Spectra of TiO_2 and TiO_2 after 2 h of irradiation look almost identical. These results support hypothesis that 2 h of aqueous as well as river solutions of OLA irradiation under solar simulated light lead to the decomposition of that pharmaceutical.

3.4.1. Photodegradation kinetics

Many reports [15,26,32] have indicated that the kinetic model for heterogeneous photocatalysis follows the Langmuir–Hinshelwood kinetic expression:

$$-\frac{d[\text{OLA}]}{dt} = \frac{kK_{\text{OLA}}[\text{OLA}]_0}{1 + K_{\text{OLA}}[\text{OLA}]_0} = k_{\text{app}}[\text{OLA}]_0 \quad (3)$$

where $[\text{OLA}]_0$ is the initial concentration of OLA [mol/L], K_{OLA} is the Langmuir–Hinshelwood adsorption equilibrium constant [L/mol], k is the rate constant of the surface reaction [mol/L min], k_{app} is the pseudo-first order rate constant.

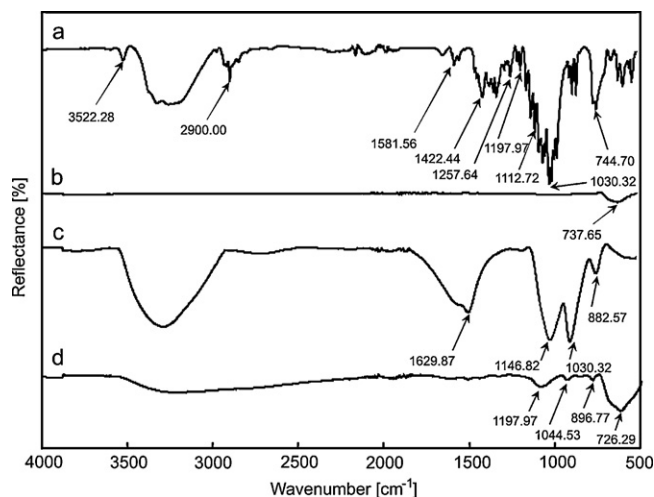


Fig. 9. ATR spectra of OLA (a), TiO_2 (b), TiO_2 after adsorption of OLA (c) and TiO_2 after 2 h of irradiation under solar simulated light (d).

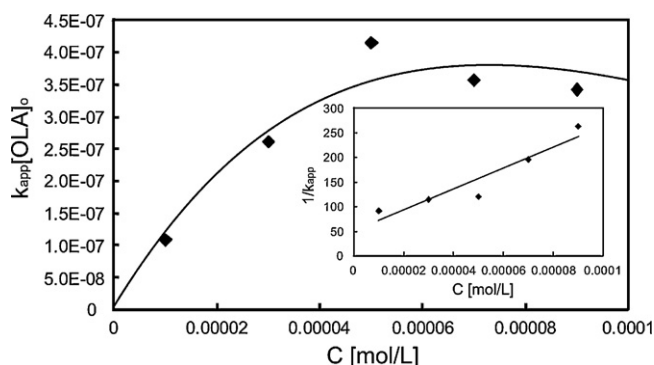


Fig. 10. Effect of initial OLA concentration on the initial rate of degradation. The inset represents the plot of $1/k_{app}$ versus initial concentration of OLA.

A linear expression can be conventionally obtained by plotting the reciprocal initial rate constant against initial concentration:

$$\frac{1}{k_{app}} = \frac{1}{kK_{OLA}} + \frac{[OLA]_0}{k} \quad (4)$$

The effect of initial OLA concentration on the initial rate of degradation is shown in Fig. 10. The figure indicates that the rate of decomposition increases with the increasing initial concentration of OLA which corresponds to Langmuir–Hinshelwood adsorption model, in spite of the fact, that adsorption of OLA was turned to be physical. It should be assumed to the complexity of the heterogeneous photocatalysis and the influence of many factors and their mutual effects.

According to Eq. (4), $1/k_{app}$ versus $[OLA]_0$, as shown in the inset in Fig. 10, gives a linear relationship. From the values of the slope $1/k$ and the intercept $1/kK_{OLA}$, k and K_{OLA} values for the photocatalytic degradation of OLA were found to be respectively 0.472 mol/L min and 0.0876 L/mol.

Integration of Eq. (3) (with the restriction of $C = C_0$ at $t = 0$) will lead to the following relation:

$$\ln \frac{C_0}{C_t} = k_{app} t \quad (5)$$

The plot of $\ln(C_0/C_t)$ versus t was used for the estimation of the pseudo-first order rate constant, k_{app} , and the half-life, $t_{1/2}$, of the photocatalytic degradation of OLA (Table 4). The decrease in k_{app} and increase in $t_{1/2}$ were observed while OLA concentration was rising. All the subsequent photolytic as well as photocatalytic degradation experiments were performed using 50 μ M OLA solutions.

3.4.2. Effect of irradiation source

Influence of an irradiation source on the efficiency of a photodegradation process was examined. Calculated k_{app} and $t_{1/2}$ values were presented in Table 5.

To our surprise, the photocatalytic activity of TiO_2 for the degradation of OLA was found to be higher in case of solar simulated light in comparison with ultraviolet radiation. However, the expecting correlation of wavelength in case of UV radiation and

Table 4

Pseudo-first order rate constants k_{app} and half-live times $t_{1/2}$ for photocatalytic degradation of OLA upon irradiation with solar simulated light (250 W/m²) at varying OLA concentration (μ M).

OLA concentration (μ M)	k_{app} (min ⁻¹)	$t_{1/2}$ (min)
10	0.0109	64
30	0.0087	80
50	0.0083	84
70	0.0051	136
90	0.0038	182

Table 5

Pseudo-first order rate constants k_{app} and half-live times $t_{1/2}$ for the photocatalytic degradation of OLA upon irradiation with solar simulated light (with intensity of 250 and 500 W/m²) and monochromatic ultraviolet lamp (of 256 and 366 nm).

Irradiation source	Experiment conditions	k_{app} (min ⁻¹)	$t_{1/2}$ (min)
SUNTEST	$E = 250$ W/m ² , pH 2	0.0097	71
SUNTEST	$E = 250$ W/m ² , pH 7	0.0083	84
SUNTEST	$E = 250$ W/m ² , pH 10	0.0064	108
SUNTEST + filter	$E = 250$ W/m ² , pH 7	0.0062	112
SUNTEST	$E = 500$ W/m ² , pH 7	0.0102	68
UV	$\lambda = 254$ nm, pH 7	0.0075	92
UV	$\lambda = 366$ nm, pH 7	0.0065	107
UV + filter	$\lambda = 366$ nm, pH 7	0.0046	151

the intensity in the event of solar simulated light was retained. Namely, as values of k_{app} and $t_{1/2}$ presented in Table 2 show, the rate of the photocatalytic process of OLA degradation increases in the following order: UV ($\lambda = 366$ nm) < UV ($\lambda = 254$ nm) < SUNTEST ($E = 250$ W/m²) < SUNTEST ($E = 500$ W/m²). The reason of a higher efficiency of a photodegradation process in case of solar simulated light might be the higher values of energy dose of that irradiation source as actinometric measurements revealed.

3.4.3. Effect of a filter presence

The influence of an UV filter presence on the photocatalytic degradation of OLA upon irradiation with a solar light simulator as well as ultraviolet lamp was studied. Pseudo-first order rate constants k_{app} and half-live times $t_{1/2}$ for the photocatalytic degradation of OLA upon irradiation with solar simulated light (250 W/m²) and an ultraviolet lamp (366 nm) in UV filter presence were presented in Table 5.

Results showed that the presence of UV filter decreases k_{app} and, as a consequence, increases $t_{1/2}$. k_{app} values obtained upon irradiation with solar simulated light with UV filter presence and upon ultraviolet light without using filter were similar. The photodegradation rate was the highest in case of an application of solar simulated light without a filter, while it reached the lowest level when ultraviolet radiation with UV filter was applied.

3.4.4. Effect of pH

The efficiency of the photocatalytic processes strongly depends on the pH of the reaction solution. Hoffman et al. [33] concluded that the interpretation of TiO_2 with cationic electron donors and electron acceptors would be favored for heterogeneous photocatalytic activity at high pH greater than the zero point charge (ZPC) of TiO_2 (~4.5), while anionic electron donors and electron acceptors would be favored at low pH less than the ZPC of TiO_2 . Therefore, an appropriate solution pH is needed for photocatalytic reactions [34].

The results presented in Table 5 revealed that photodegradation efficiency of TiO_2 decreased in order of pH 2 > pH 7 > pH 10. Findings of others also show that degradation of anionic compounds is more in acidic medium because at pH higher than ZPC of TiO_2 , its surface becomes negatively charged so adsorption will be less [35]. However, the most important factor seems to be high clarity of the examined suspension. It was obtained in acidic conditions, while in the basic environment photocatalyst formed sediments at the bottom. Therefore, highest photodegradation efficiency was achieved when experiments were performed in acidic conditions.

UV spectra of OLA solutions at different pH were already shown in Fig. 1, while spectra registered during photocatalytic degradation of OLA under different pH values (2, 7 and 10) were presented in Fig. 11. While spectra obtained from solutions of pH 2 and pH 7 were similar and typical for OLA, the spectrum registered at pH 10 was different. The absorption spectrum of OLA is characterized by one main band in the ultraviolet region at $\lambda = 256$ nm. Whereas under

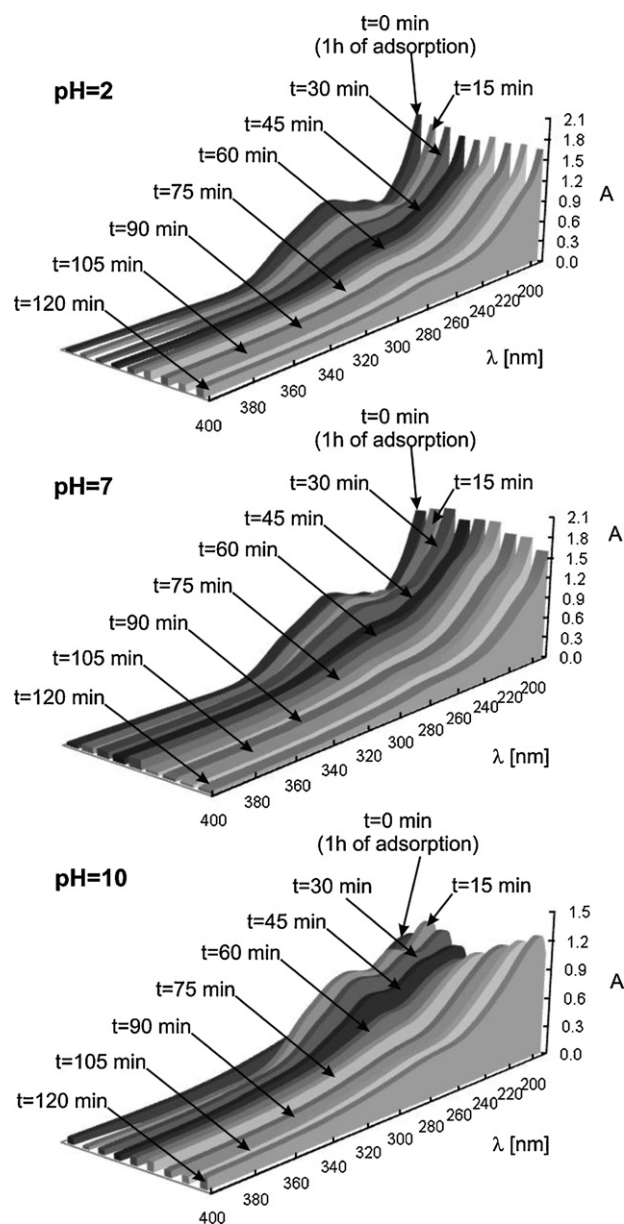


Fig. 11. UV spectra during photocatalytic degradation of OLA under pH 2, 7 and 10.

pH 10 two additional bands, at 196 and 222 nm, appeared. Those differences result from different protonated forms of OLA. That pharmaceutical is a base possessing four nitrogen atoms among which two can be protonated during decreasing pH value and one is permanently bonded to hydrogen.

3.4.5. OLA degradation in river waters

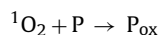
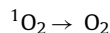
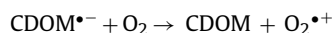
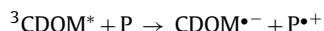
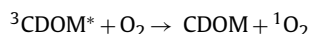
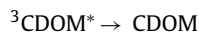
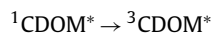
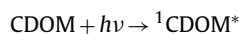
Photodegradation experiments of OLA in river suspension of TiO_2 were performed. With the aim of doing that, two solutions of OLA were prepared. Water from two rivers, namely Marycha and Narew, was used for that purpose. Two irradiation sources: ultraviolet and solar simulated light, were used in that case too. Obtained results were presented in Fig. 12.

As Fig. 12 depicts, application of solar simulated light led to higher photodegradation efficiencies than use of ultraviolet radiation. It is true in case of photolytic (Fig. 12a and c) as well as photocatalytic (Fig. 12b and d) experiments. However, differences are definitely greater in case of a photolysis. Photodegradation efficiencies in OLA solutions of both rivers achieved 100% under

irradiation using solar simulated light, while application of ultraviolet radiation after 2 h led to 5 and 11% of degradation in case of Marycha and Narew, respectively.

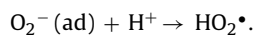
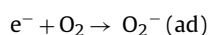
Introduction of a photocatalyst to the pharmaceutical solution in both rivers significantly enhanced photocatalytic efficiency. Taking into account experiments conducted under solar simulated light the differences in percentage of degradation were noticeable in case of 1 h of irradiation. They changed from 29 to 75 and from 72 to 100% in case of OLA solutions in Marycha and Narew waters. While application of ultraviolet light led to significant changes in photodegradation efficiency after 1 and 2 h of irradiation. In Marycha solution percentage of OLA degradation changed from 2 to 29 and from 5 to 60 in case of 1 and to 2 h of irradiation, respectively. Introduction a photocatalyst to the Narew solutions of OLA led to the enhancement of pharmaceutical degradation from 3 to 24 and from 11 to 88% after 1 and 2 h of irradiation, respectively. Nevertheless, in none of those cases (with application of ultraviolet light) complete disappearance of studied pharmaceutical was observed.

Higher photodegradation efficiencies of OLA obtained in case of river waters can be explained taking into consideration their constituents. Natural waters contain chromophores that take part in a variety of photochemical reactions involving and producing reactive species that can initiate the degradation of the target contaminant. The so called colored dissolved organic matter (CDOM) is a precursor of different reactive species including $^1\text{O}_2$ and $^3\text{CDOM}^*$ that could be more important than HO^\bullet . CDOM after exposing to the solar light undergoes following reactions [36]:

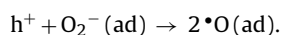
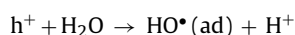


where P is the phenol or its derivative.

OLA was degraded less efficiently in the water from Marycha, which demonstrated lower oxygen demand and higher Fe concentration as well as general hardness. Oxygen takes part in above shown reactions and is also a source of oxygen radicals. It can be adsorbed on the photocatalyst surface and undergoes following reactions on the conduction band of TiO_2 :



The valence band of TiO_2 supplies other forms of active oxygen as a consequence of the following processes:



Oxygen, in above mentioned forms, like O_2^- , HO^\bullet , HO_2^\bullet and $^\bullet\text{O}$ may be responsible for the decomposition reactions [37].

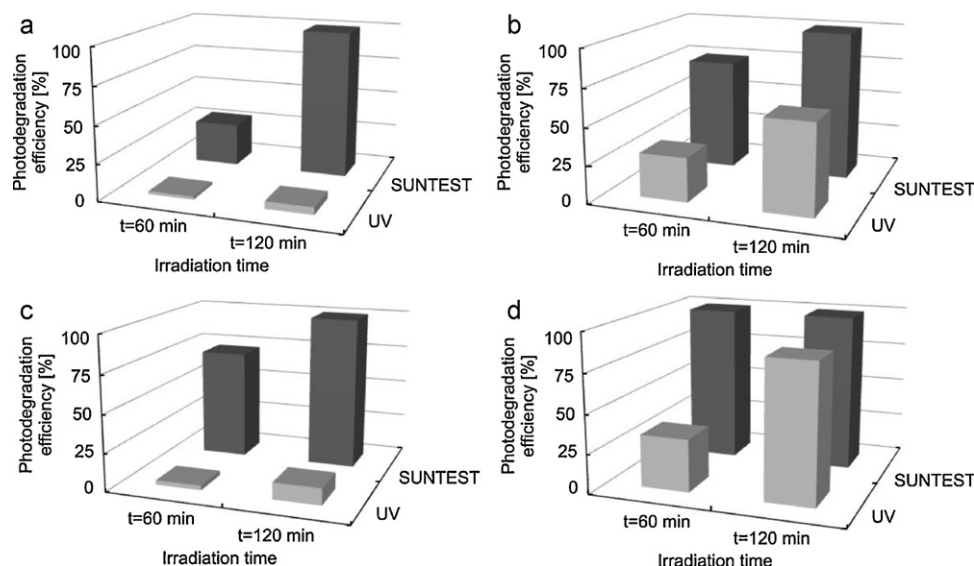
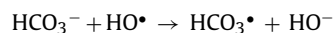
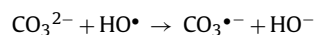


Fig. 12. Photodegradation efficiencies obtained after photolysis and photocatalysis in Marycha (a and b, respectively) and Narew (c and d, respectively) solutions of OLA using ultraviolet (UV) and solar simulated light (SUNTEST).

The presence of Fe cations was proved to decrease the photocatalytic degradation rates by others [38]. Therefore, we also attribute the higher Fe concentration in case of Marycha to its negative influence on the photodegradation process of OLA.

Higher general hardness in case of Marycha river has also a negative influence on the photocatalytic decomposition of OLA. General hardness relates to the content of carbonate and bicarbonate ions. Those ions react with HO^\bullet forming less active radicals, as given below:



All above presented reactions explain higher photodegradation efficiencies of OLA obtained in river waters in compare with aqueous solutions as well as better decomposition in case of Marycha water in compare with Narew water.

4. Conclusions

Studied pharmaceutical was found to be resistant to photolytic decomposition in aqueous environment, but it undergoes the photolytic degradation in solutions of river waters. However, the highest photodegradation efficiencies were obtained during photocatalytic experiments. Those studies were performed in the suspension of TiO_2 . 2 h of irradiation upon both ultraviolet and solar simulated light led to the total decomposition of OLA with the formation of low molecular species. In summary, we realized the application of heterogeneous photocatalysis for olanzapine removal from aquatic environment. Therefore, the current research can be considered as a step towards the commercialization of the photocatalytic removal of olanzapine from river waters.

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